

## Claims

Claims for the following Contracting States : AT, BE, CH, DE, FR, GB, GR, IT, LI, LU, NL, SE

1. Multilayer composite interpolymers comprising at least:
  - an elastomeric internal stage which in itself has a glass transition temperature lower than or equal to 25 ° C, polymerised by starting with a mixture comprising, per 100 parts by weight:
    - (a) from 50 to 99.9 parts by weight of at least one main monomer chosen from conjugated dienes and alkyl or aralkyl acrylates;
    - (b) from 0 to 49.9 parts by weight of at least one other monomer containing monoethylenic saturation copolymerisable with the said main monomer;
    - (c) from 0.05 to 8 parts by weight of at least one crosslinking monomer; and
    - (d) from 0.05 to 6 parts by weight of at least one grafting monomer; and
  - a relatively hard, nonelastomeric external stage which in itself has a glass transition temperature higher than 25 ° C, polymerised in the presence of the product of the preceding stage, by starting with a mixture comprising, per 100 parts by weight:
    - (a) from 50 to 99.9 parts by weight of at least one main monomer chosen from alkyl methacrylates in which the alkyl group contains from 1 to 4 carbon atoms, vinylaromatic hydrocarbons and unsaturated nitriles;
    - (b) from 0.1 to 50 parts by weight of at least one monomer containing monoethylenic unsaturation copolymerisable with the said main monomer, and
    - (c) from 0 to 5 parts by weight of at least one chain limiter agent,

characterised in that it has a bimodal particle distribution and that it consists of a mixture:

  - (1) of a population of particles whose mean diameter is between approximately 40 and 150 nm; and
  - (2) a population of particles whose mean diameter is between approximately 160 and 500 nm,

in a weight ratio of the population (1) to the population (2) of between approximately 5/95 and approximately 95/5.
2. Interpolymer according to Claim 1, characterised in that at least a fraction of the particles of which it consists comprises a relatively hard, nonelastomeric first stage forming the core of the particles, which has a glass transition temperature higher than 25 ° C, polymerised by starting with a mixture comprising, per 100 parts by weight,
  - (a) from 70 to 99.9 parts by weight of at least one main monomer chosen from alkyl methacrylates in which the alkyl group contains from 1 to 4 carbon atoms, vinylaromatic hydrocarbons and unsaturated nitriles;
  - (b) from 0.1 to 10 parts by weight of at least one other monomer containing monoethylenic unsaturation copolymerisable with the said main monomer;
  - (c) from 0 to 10 parts by weight of at least one crosslinking monomer; and
  - (d) from 0 to 10 parts by weight of at least one grafting monomer,

the internal and external stages constituting the second and third stages of the interpolymer particles respectively.
3. Interpolymer according to Claim 1, characterised in that at least a fraction of the particles of which it consists comprises a relatively soft elastomeric first stage forming the core of the particles, which has a glass transition temperature lower than or equal to 25 ° C, polymerised, in the absence of any crosslinking monomer or grafting monomer, by starting with a mixture comprising, per 100 parts by weight:
  - (a) from 50 to 100 parts by weight of at least one main monomer chosen from conjugated dienes and alkyl or aralkyl acrylates; and
  - (b) from 0 to 50 parts by weight of at least one other monomer containing ethylenic unsaturation copolymerisable with the said main monomer,

the internal and external stages constituting the second and third stages of the interpolymer particles respectively.
4. Interpolymer according to Claim 1, characterised in that the internal and external stages represent, per 100 parts by weight of the interpolymer of each population, 0.5 to 90 parts by weight and 99.5 to 10 parts by weight respectively.

5. Interpolymer according to Claim 2, characterised in that the first, second and third stages of particles of hard-soft-hard morphology represent, per 100 parts by weight of the interpolymer of each population, from 10 to 40 parts by weight, from 20 to 60 parts by weight and from 10 to 70 parts by weight respectively.
6. Interpolymer according to Claim 3, characterised in that the first, second and third stages of particles of soft-soft-hard morphology represent, per 100 parts by weight of the interpolymer of each population, 3 to 80 parts by weight, 10 to 60 parts by weight and 10 to 60 parts by weight respectively.
7. Interpolymer according to one of Claims 1 to 6, characterised in that the monomers containing monoethylenic unsaturation forming part of the definition of (b) of a nonelastomeric stage are chosen from alkyl acrylates, alkoxy acrylates, cyanoethyl acrylate, acrylonitrile, acrylamide, hydroxyalkyl acrylates, hydroxyalkyl methacrylates, acrylic acid and methacrylic acid.
8. Interpolymer according to one of Claims 1 to 7, characterised in that the monomers containing monoethylenic unsaturation forming part of the definition of (b) of an elastomeric stage are chosen from alkyl methacrylates, alkoxy acrylates, cyanoethyl acrylate, acrylonitrile, acrylamide, hydroxyalkyl acrylates, hydroxyalkyl methacrylates, acrylic acid, methacrylic acid and vinylaromatic hydrocarbons.
9. Interpolymer according to one of Claims 1 to 8, characterised in that the crosslinking monomers forming part of the definition of (c) of a core stage or of an intermediate stage are chosen from polyol polymethacrylates and polyacrylates, polyvinylbenzenes and vinyl acrylate and methacrylate.
10. Interpolymer according to one of Claims 1 to 8, characterised in that the grafting monomers forming part of the definition of (d) of a core stage, or of an intermediate stage, are chosen from allyl, methallyl or crotyl esters of  $\alpha,\beta$ -unsaturated carboxylic acids or diacids, allyl ether, methallyl ether and crotyl vinyl ether, allyl thioether, methallyl thioether and crotyl vinyl thioether, N-allyl-, methallyl- or crotyl-maleimide, vinyl esters of 3-butenic acid and of 4-pentenoic acid, triallyl cyanurate; O-allyl, methallyl or crotyl O-alkyl, aryl, alkaryl or aralkyl P-vinyl, allyl or methallyl phosphonate, triallyl, trimethallyl or tricrotyl phosphate, O-vinyl, O,O-diallyl, dimethallyl or dicrotyl phosphate, cycloalkenyl esters of acrylic acid, of methacrylic acid, of maleic acid, of fumaric acid, of itaconic acid, bicyclo[2.2.1]hept-5-en-2-yl esters of acrylic acid, of methacrylic acid, of maleic acid, of fumaric acid and of itaconic acid; vinyl ethers and vinyl thioethers of cycloalkenols and cycloalkenethiols, and the vinyl esters of cycloalkenecarboxylic acids.
11. Interpolymer according to one of Claims 1 to 10, characterised in that the chain limiter agents forming part of the definition of (c) of a final stage are chosen from mercaptans, polymercaptans, polyhalogenated compounds, diunsaturated monoterpenes and monounsaturated diterpenes.
12. Composite interpolymer according to one of Claims 1 to 11, characterised in that it is in the form of a latex with a concentration of 20 to 50 % by weight in water.
13. Composite interpolymer according to one of Claims 1 to 11, characterised in that it is in the form of a powder.
14. Process for the preparation of an interpolymer as defined in one of Claims 1 to 13, characterised in that it consists in
  - forming separately, by polymerisation, a seed consisting of the internal stage(s) of the populations (1) and (2);
  - mixing the two seeds obtained in the preceding step;
  - adding the charge of the monomers corresponding to the external stage and subjecting it to polymerisation conditions,
 each polymerisation being performed in emulsion, in an aqueous medium, in the presence of at least one free-radical initiator and of at least one emulsifying agent.
15. Thermoplastic composition consisting of a mixture comprising, per 100 parts by weight:
  - from 10 to 99 parts by weight of a rigid thermoplastic polymer of at least one monomer chosen from alkyl methacrylates in which the alkyl group contains from 1 to 4 carbon atoms, and

vinylaromatic hydrocarbons, or of a polymer of more than 50 % by weight of at least one of these monomers and of at least one other copolymerisable monomer containing monoethylenic unsaturation; and

- from 90 to 1 parts by weight of an interpolymer as defined in one of Claims 1 to 13.

16. Thermoplastic composition according to Claim 15, characterised in that the elastomeric part of the thermoplastic material present in the said composition represents from 18 to 40 parts by weight of the latter.

17. Any shaped article obtained by means of the thermoplastic composition as defined in either of Claims 15 and 16.

**Claims for the following Contracting State : ES**

1. Process for the preparation of a multilayer composite interpolymer characterised in that it consists in:

- preparing sequentially, by polymerisation in emulsion, in an aqueous medium, in the presence of a free-radical initiator and of an emulsifying agent, populations (1) and (2) of particles of the said multilayer composite interpolymer, which comprises at least:
  - an elastomeric internal stage which in itself has a glass transition temperature lower than or equal to 25 °C, which is polymerised by starting with a mixture comprising, per 100 parts by weight:
    - (a) from 50 to 99.9 parts by weight of at least one main monomer chosen from conjugated dienes and alkyl or aralkyl acrylates;
    - (b) from 0 to 49.9 parts by weight of at least one other monomer containing monoethylenic unsaturation copolymerisable with the said main monomer;
    - (c) from 0.05 to 8 parts by weight of at least one crosslinking monomer; and
    - (d) from 0.05 to 6 parts by weight of at least one grafting monomer; and
  - a relatively hard, nonelastomeric external stage which in itself has a glass transition temperature higher than 25 °C, which is polymerised in the presence of the product of the preceding stage, by starting with a mixture comprising, per 100 parts by weight:
    - (a) from 50 to 99.9 parts by weight of at least one main monomer chosen from alkyl methacrylates in which the alkyl group contains from 1 to 4 carbon atoms, vinylaromatic hydrocarbons and unsaturated nitriles;
    - (b) from 0.1 to 50 parts by weight of at least one monomer containing monoethylenic unsaturation copolymerisable with the said main monomer, and
    - (c) from 0 to 5 parts by weight of at least one chain limiter agent,
- the particles of the population (1) having a mean diameter of between approximately 40 and 150 nm, and those of the population (2), a mean diameter of between approximately 160 and 500 nm; and
- mixing the populations (1) and (2) of particles in a weight ratio of population (1) to population (2) of between approximately 5/95 and approximately 95/5, to obtain a multilayer composite interpolymer comprising a bimodal particle distribution.

2. Process for the preparation of a multilayer composite interpolymer, characterised in that it consists in:

- forming separately, by polymerisation, a seed consisting of the internal stage(s) of a particle population (1) and the external stage(s) of a particle population (2), each internal stage being an elastomeric stage having in itself a glass transition temperature lower than or equal to 25 °C, which is polymerised by starting with a mixture comprising, per 100 parts by weight:
  - (a) from 50 to 99.9 parts by weight of at least one main monomer chosen from conjugated dienes and alkyl or aralkyl acrylates;
  - (b) from 0 to 49.9 parts by weight of at least one other monomer containing monoethylenic unsaturation copolymerisable with the said main monomer;
  - (c) from 0.05 to 8 parts by weight of at least one crosslinking monomer; and
  - (d) from 0.05 to 6 parts by weight of at least one grafting monomer;
- mixing the two seeds obtained in the preceding step;
- adding the charge of the monomers corresponding to a relatively hard, nonelastomeric external stage having in itself a glass transition temperature higher than 25 °C, which is polymerised in the presence of the product of the preceding stage, by starting with a mixture comprising, per 100 parts by weight: